Active and Durable PGM-free Cathodic Electrocatalysts for Fuel Cell Application

PI: Alexey Serov

Pajarito Powder, LLC

aserov@pajaritopowder.com

Co-PIs: Tatyana Reshetenko (HNEI) and Madeleine Odgaard (IRD Fuel Cells)

May 28, 2020

Project ID # FC305

Overview

Timeline

- Project Start Date: 01/01/19
- Project End Date: 12/31/20

Barriers

- Activity of PGM-free ORR catalysts should be increased
- Decrease a cost of PGM-free catalysts manufacturing
- Increase the durability PGM-free catalysts

Budget

- Total DOE Funds Spent to Date: $487,983.61
- Total DOE Project Value: $999,814.00

Partners

- IRD Fuel Cells, Madeleine Odgaard
- University of Hawaii, Hawaii Natural Energy Institute (HNEI), Dr. Tatyana Reshetenko

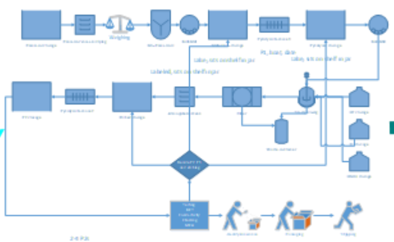
Relevance: Objectives and Targets

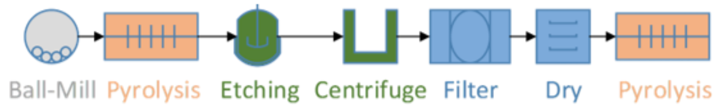
- Objectives: Development of PGM-free electrocatalysts for ORR; the catalysts will be scaled up to 50g batches (PP); PGM-free catalysts will be integrated into the industrial state-of-the-art MEAs (IRD) and comprehensively evaluated by electrochemical methods (HNEI).

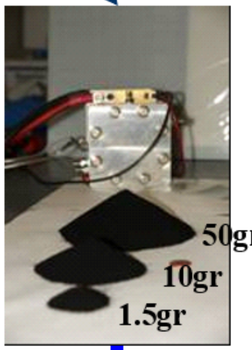
- Relevance to DOE Mission: Inexpensive, highly active and stable PGM-free ORR catalysts commercially manufactured by US catalyst company will demonstrate required by DOE performance level due to understanding the electrochemical processes relevant to **PGM-free** materials in mass-produced MEAs.

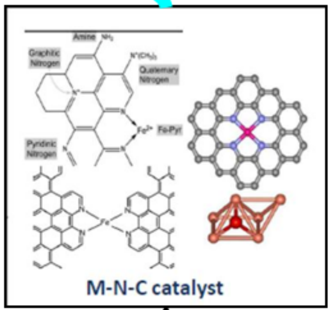
- Targets
  - Demonstrate 0.044 A/cm^2 at 0.9V (iR-free, H_2/O_2 configuration, 1bar O_2, 80ºC, 100%RH)

Approach: Catalysts and Method

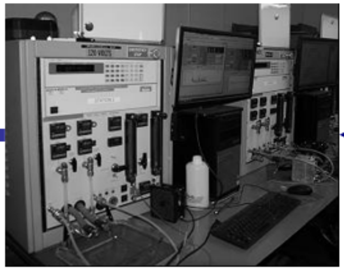


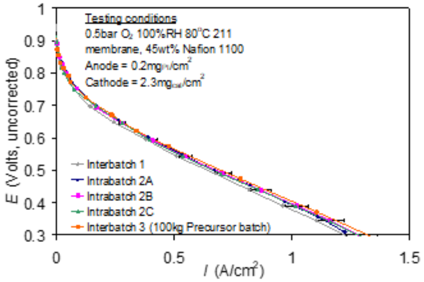






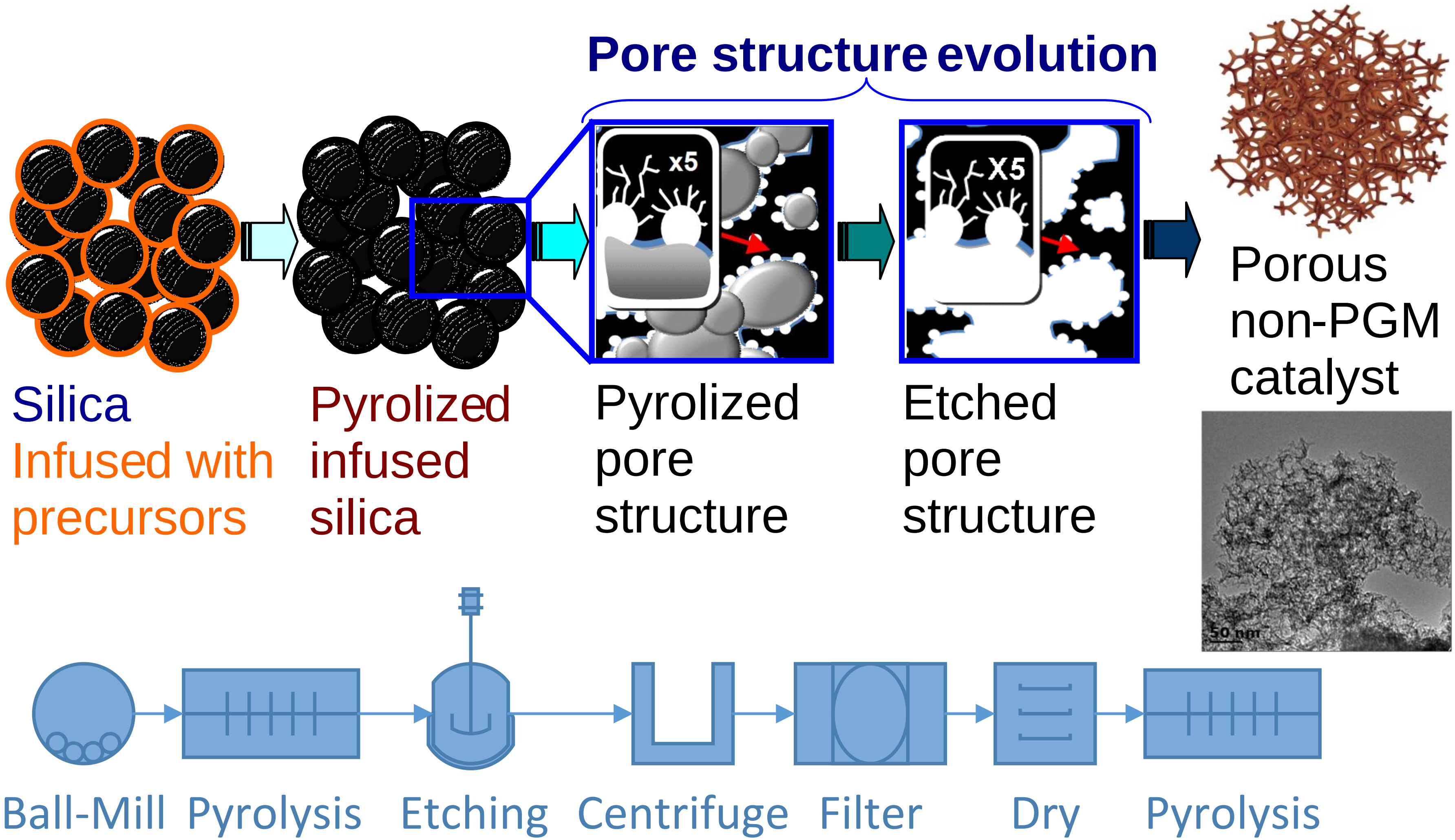
Pajarito Powder is able to manufacture up to 200g of PGM-free ORR catalysts per batch





US20080312073A1,WO2012174335A2,WO2013116754A1,WO2012174344A2,WO2014062639A1,WO2014011831A1,WO2014085563A1,WO2014113525A1,

Approach: VariPore™ Method



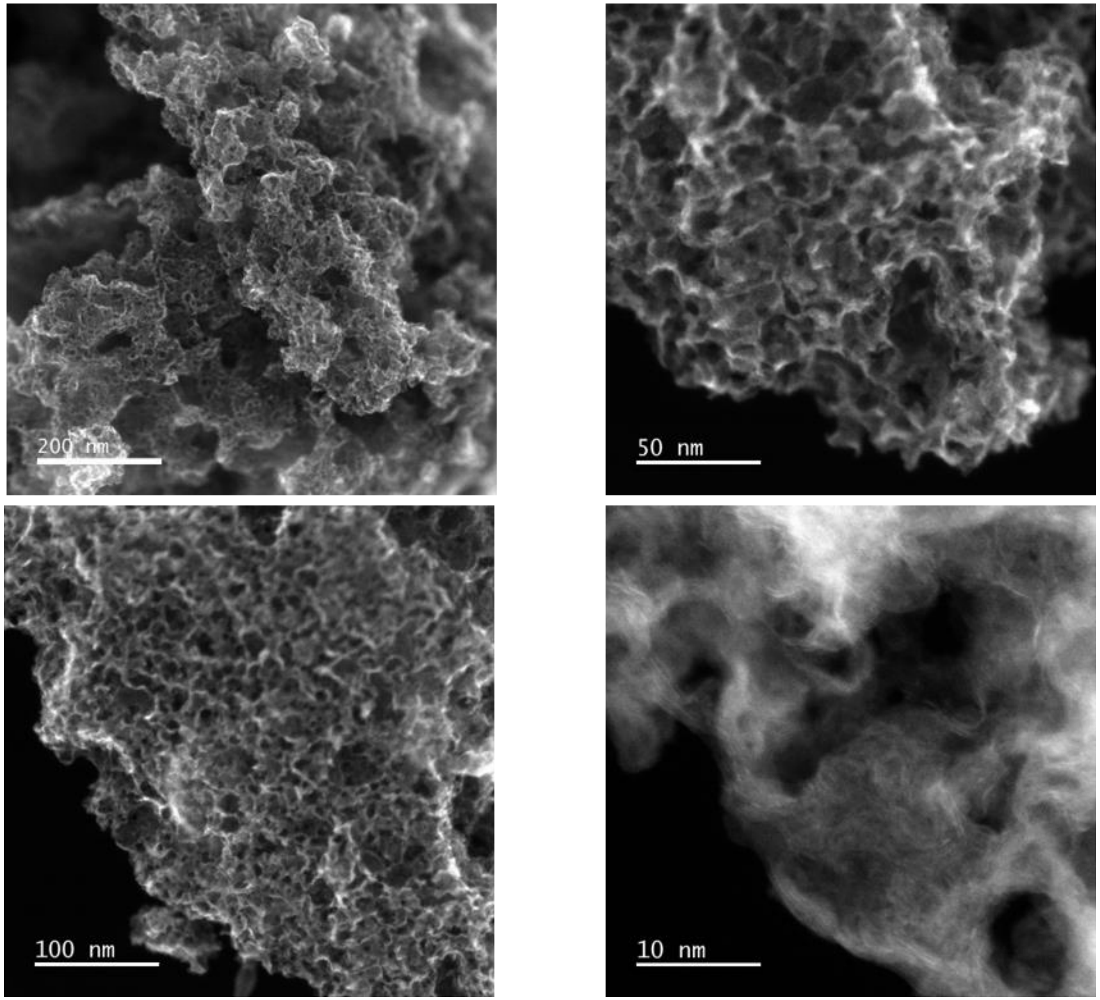
Approach: Timeline and Milestones

Milestone Schedule							
Milestone #	Project Milestones	Type	Task Completion Date (Project Quarter)				Progress Notes
			Original Planned	Revised Planned	Actual	Percent Complete	
1.1	Correlation between synthesis parameters and morphology and chemistry of catalyst	Milestone	4/30/2019		4/30/2019	100%	Gen-1 is characterized by XRD, BET and Raman
1.2	Deliver 10 MEAs with stock catalyst	Milestone	4/30/2019		4/30/2019	100%	Delivered to PP and HNEI
1.3	Activity will be compared with preliminary data obtained at Pajarito Powder: 0.025 A/cm2 at 0.83V (iR-free), with H2 /O2 at 1.0 bar O2, 100%RH, 80 °C	Milestone	4/30/2019		3/30/2019	100%	PP manufactured MEAs which achieved Milestone performance.
2.1	Deliver Gen-2 catalysts	Milestone	7/31/2019		7/15/2019	100%	Gen-2 synthesized by PP. IRD made MEAs and delivered to HNEI and PP.
2.2	Deliver 10 MEAs with Gen-2 catalyst Activity Targett: MEA that produces 0.025 A/cm2 at 0.85 V (iR-free), with H2 /O2 at 1.0 bar O2, 100%RH, 80 °C	Milestone	10/31/2019		8/10/2019	100%	MEAs were tested. Milestone is met.
2.3	Recommendation to improve catalyst	Milestone	1/31/2020			100%	Surface area of catalysts should be higher than 560 $m^2 g^{-1}$.
Go/No-Go #1	**MEA that produces 0.025 A/cm2 at 0.90 V (iR-free), with H2 /O2 at 1.0 bar O2, 100%RH, 80 °C**	**Go/No-Go**	**1/31/2020**			**100%**	**Post-treatment of catalyst in ammonia improved activity.**

Accomplishments and Progress

- **Gen-1 Catalysts Variables:** N-C precursor was fixed to Pipemidic Acid, 3 types of silica used (SA = 150, 400 and 500 $m^2\ g^{-1}$), precursors mixtures were dried differently (air-dried and vacuum-dried). Resulted in Fe-N-C type (SA ~500 $m^2\ g^{-1}$)
- **Gen-2 Catalysts Variables:** N-C precursor was fixed to Nicarbazin, 3 types of silica used (SA = 150, 400 and 500 $m^2\ g^{-1}$), precursors mixtures were dried differently (air-dried and vacuum-dried). Heat treatment temperature was higher compared to Gen-1. Resulted in Fe-N-C type (SA ~ 600 $m^2\ g^{-1}$)
- **Gen-2A Catalysts Variables:** N-C precursor was fixed to Nicarbazin, 3 types of silica used (SA = 150, 400 and 500 $m^2\ g^{-1}$), precursors mixtures were dried differently (air-dried and vacuum-dried). Samples were ammonia treated.
- **Gen-2B Catalysts Variables:** N-C precursor was fixed to Nicarbazin. ZIF-8 was used as a pore/particle former. Samples were ammonia treated.
- **Gen-3.1 Catalysts Variables:** Mn was added to Fe precursor. Resulted in Fe-Mn-N-C (SA ~700 $m^2\ g^{-1}$). Samples will be ammonia treated.
- **Gen-3.2 Catalysts Variables:** Addition of different amount of Urea to Fe-N-C, Fe-Mn-N-C and other materials to increase number of $Fe\text{-}N_x$ centers and decrease particle size of catalysts.

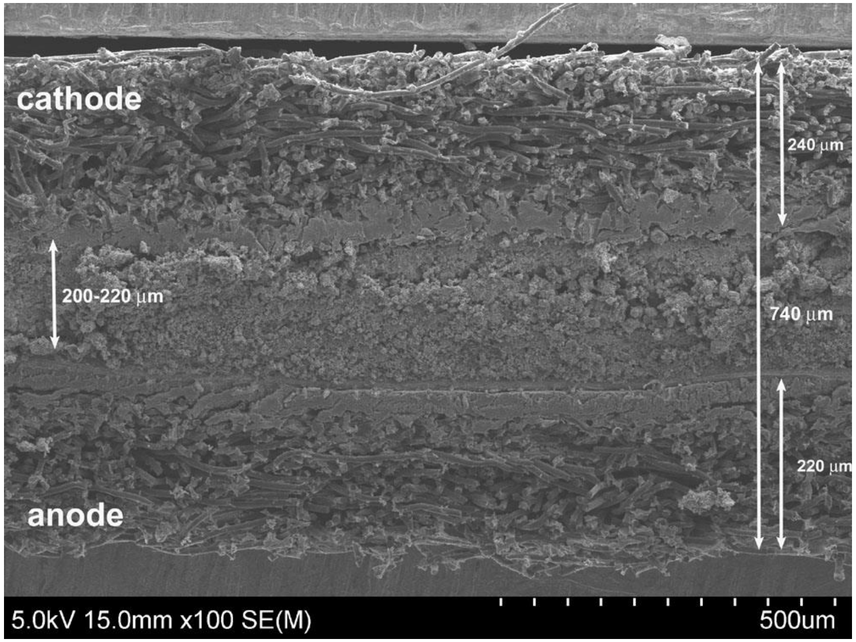
Accomplishments and Progress

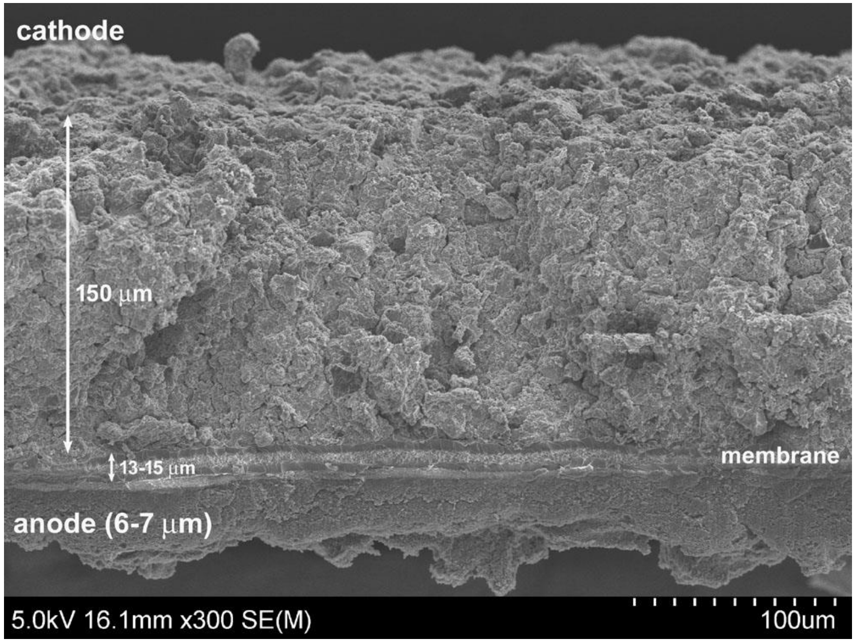


Gen-2 (non-NH_3 treated samples): high surface area silica resulted in formation of several levels of porosity.

Microscopy by Dr. David Cullen (ORNL)

Accomplishments and Progress



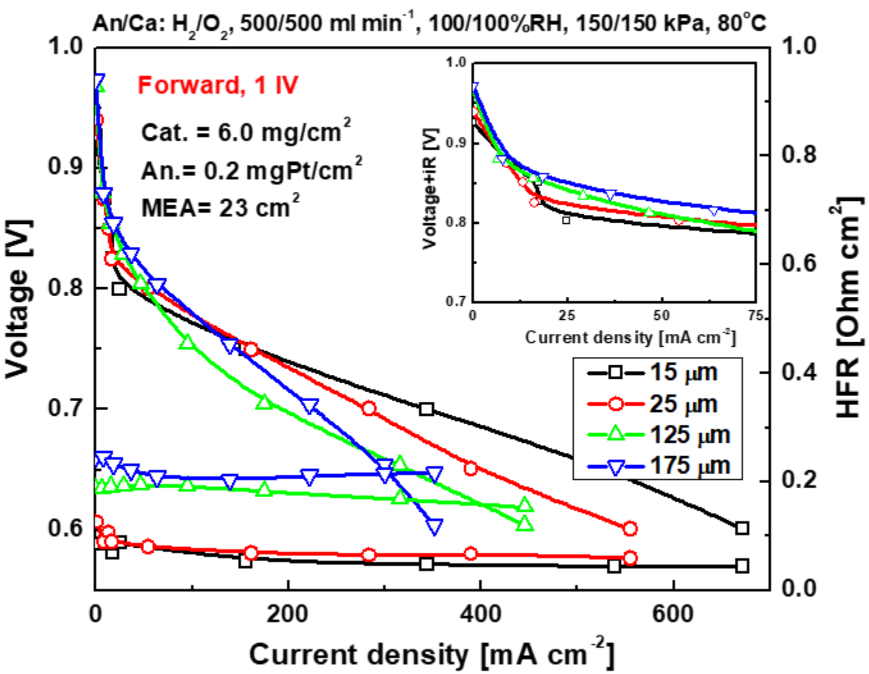


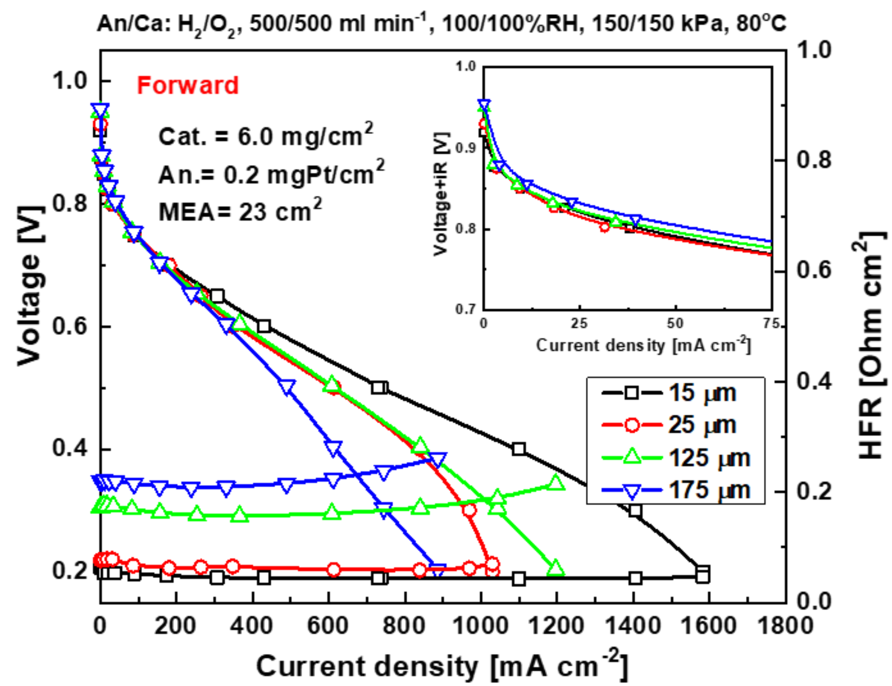
Gen-2 catalysts were integrated into 25cm^2 MEAs and evaluated at HNEI (6mg/cm^2 loading)

T. Reshetenko, G. Randolf, M. Odgaard, B. Zulevi, A. Serov, A. Kulikovsky *"The Effect of Proton Conductivity of Fe–N–C–Based Cathode on PEM Fuel cell Performance*" Journal of The Electrochemical Society 167 (2020) 084501

Accomplishments and Progress

Fuel Cell Performance of Fe-N-C Gen-2 Catalysts with Different Membranes





Highest performance was achieved using thinnest membrane - 15µm (all data non-iR$_{corrected}$)

T. Reshetenko, G. Randolf, M. Odgaard, B. Zulevi, A. Serov, A. Kulikovsky *"The Effect of Proton Conductivity of Fe–N–C–Based Cathode on PEM Fuel cell Performance"* Journal of The Electrochemical Society 167 (2020) 084501

Accomplishments and Progress

PAJARITO POWDER
FUEL CELL CATALYSTS

Fuel Cell EIS Modeling of Fe-N-C Gen-2 Catalysts with Different Membranes
Collaboration with Dr. Andrei Kulikovsky

	15 um, 50 mA/cm^2	15 um, 100 mA/cm^2	25 um, 50 mA/cm^2	25 um, 100 mA/cm^2
Tafel slope / mV/exp	36.9	42.0	39.6	39.8
Tafel slope / mV/decade	85.0	96.7	91.2	91.7
CCL proton conductivity / mS/cm	8.83	4.94	9.12	3.96
Volumetric DL capacitance / F/cm^3	14.8	19.3	10.0	22.8
CCL oxygen diffusion coeff. / 1e^{-4} cm^2/s	large	large	45.2	43.9
GDL oxygen diffusion coeff. / cm^2/s	large	large	large	0.13

Based on EIS modeling suggests low H^+ conductivity and ORR kinetics are limiting MEA performance

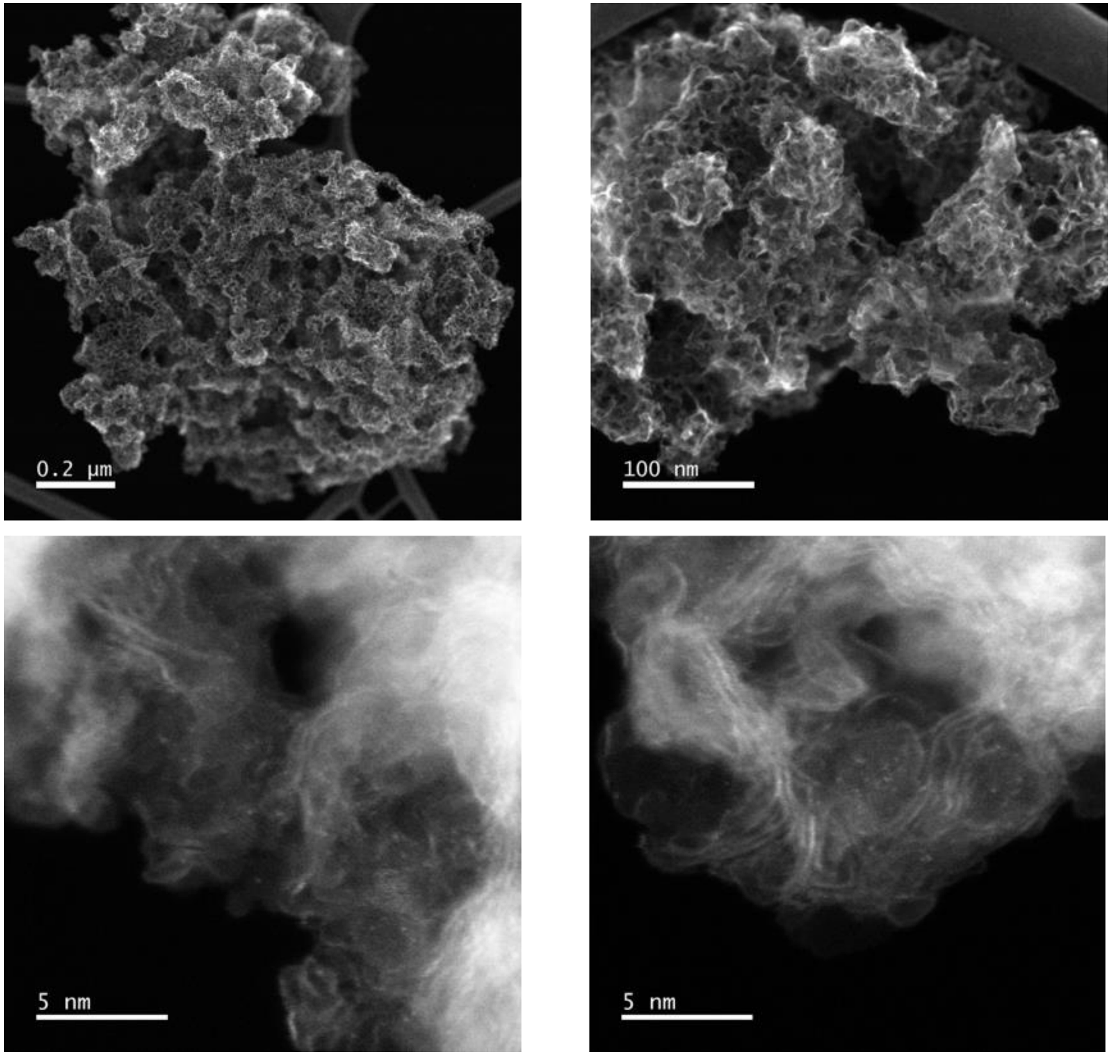
HiSERF

HAWAII SUSTAINABLE ENERGY RESEARCH FACILITY
A University of Hawaii - Hawaiian Electric Company Partnership
Sponsored by
Office of Naval Research and U.S. Department of Energy

T. Reshetenko, G. Randolf, M. Odgaard, B. Zulevi, A. Serov, A. Kulikovsky *"The Effect of Proton Conductivity of Fe–N–C–Based Cathode on PEM Fuel cell Performance"* Journal of The Electrochemical Society 167 (2020) 084501

IRD

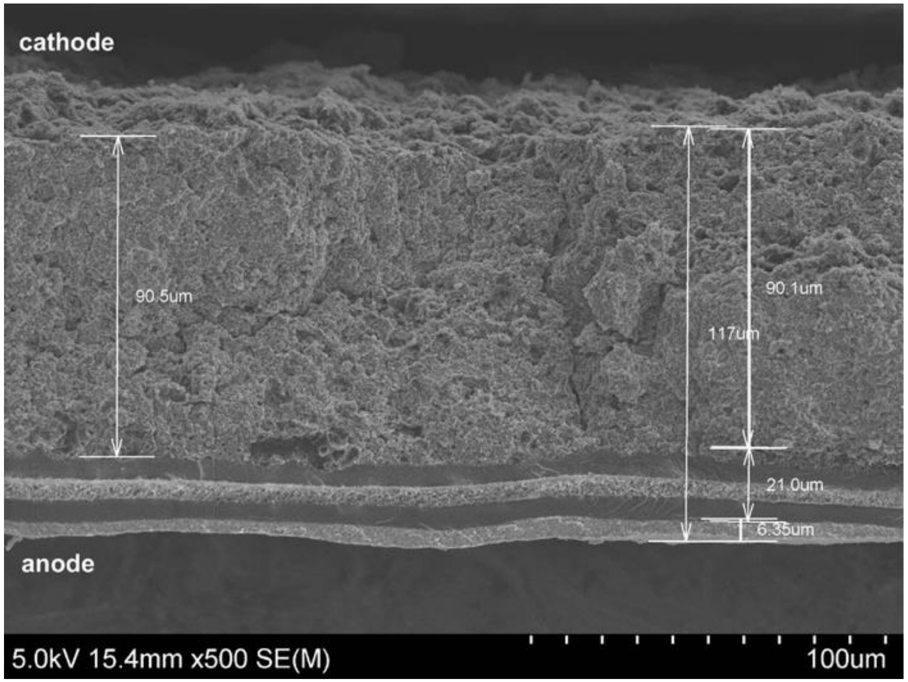
Accomplishments and Progress

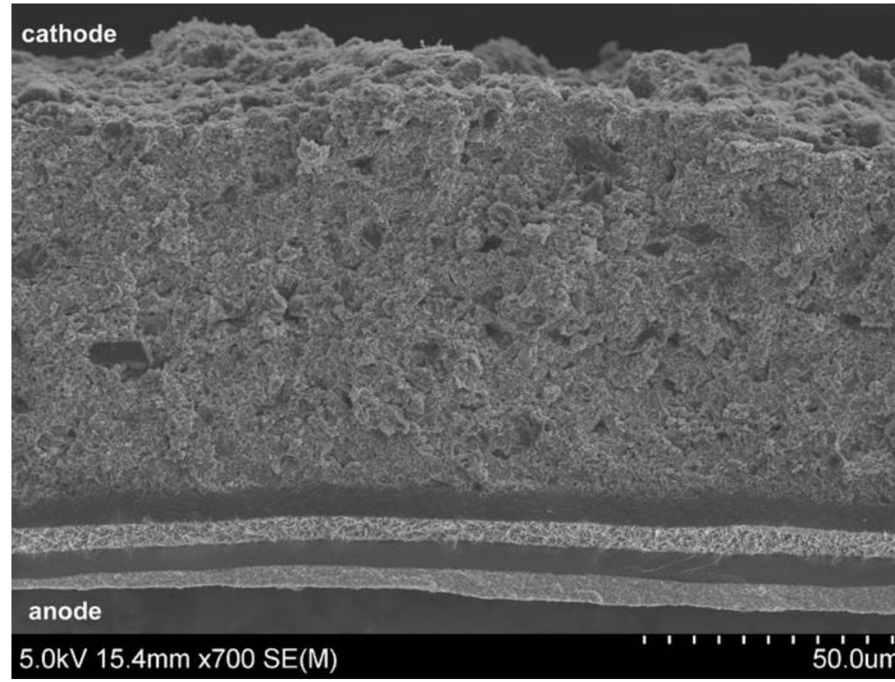


Gen-3 (NH_3 treated samples): carbon matrix substantially etched by NH_3. Atomically dispersed $Fe-N_x$ centers are exposed.

Microscopy by Dr. David Cullen (ORNL)

Accomplishments and Progress



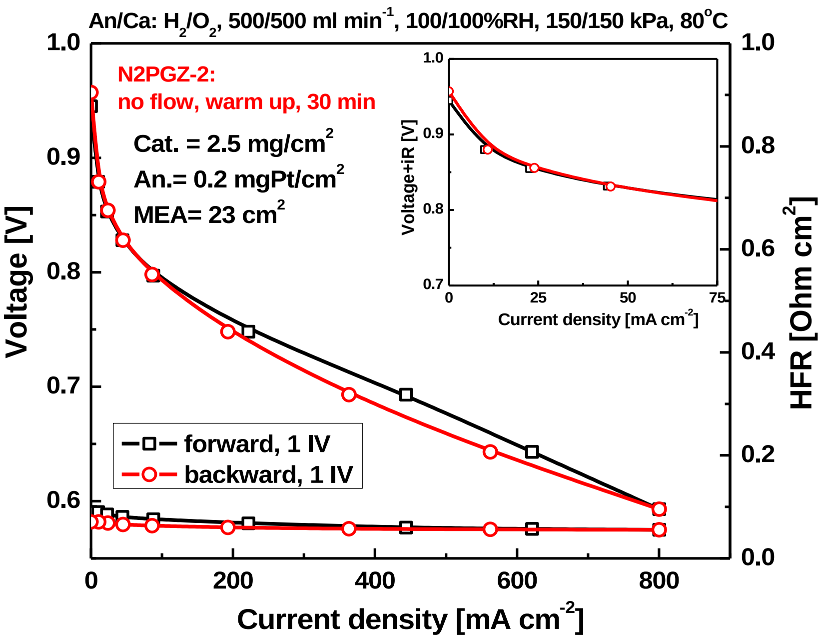


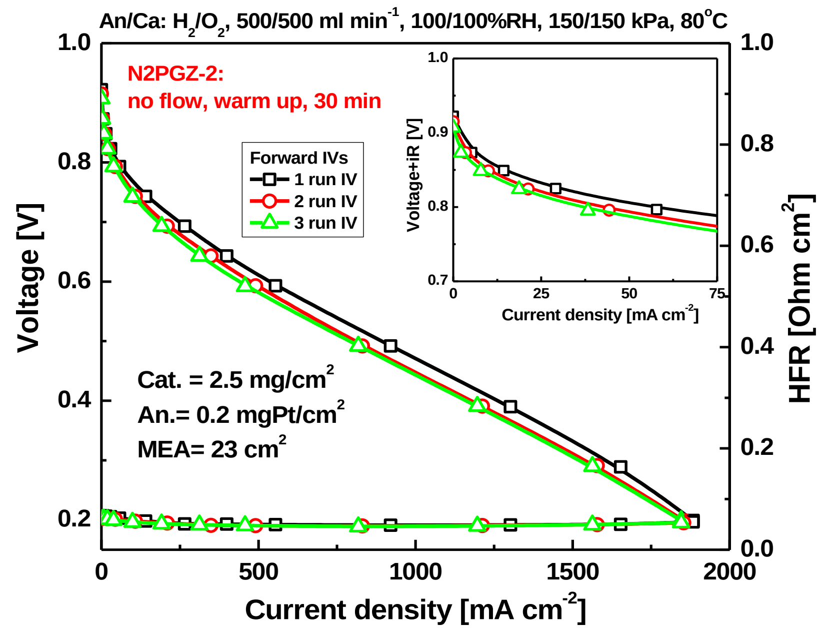
Gen-3 catalyst (2.5 mg/cm^2 loading) has much thinner catalyst layer in 25cm^2 MEA

HAWAII SUSTAINABLE ENERGY RESEARCH FACILITY
A University of Hawaii – Hawaiian Electric Company Partnership
Sponsored by
Office of Naval Research and U.S. Department of Energy

Accomplishments and Progress

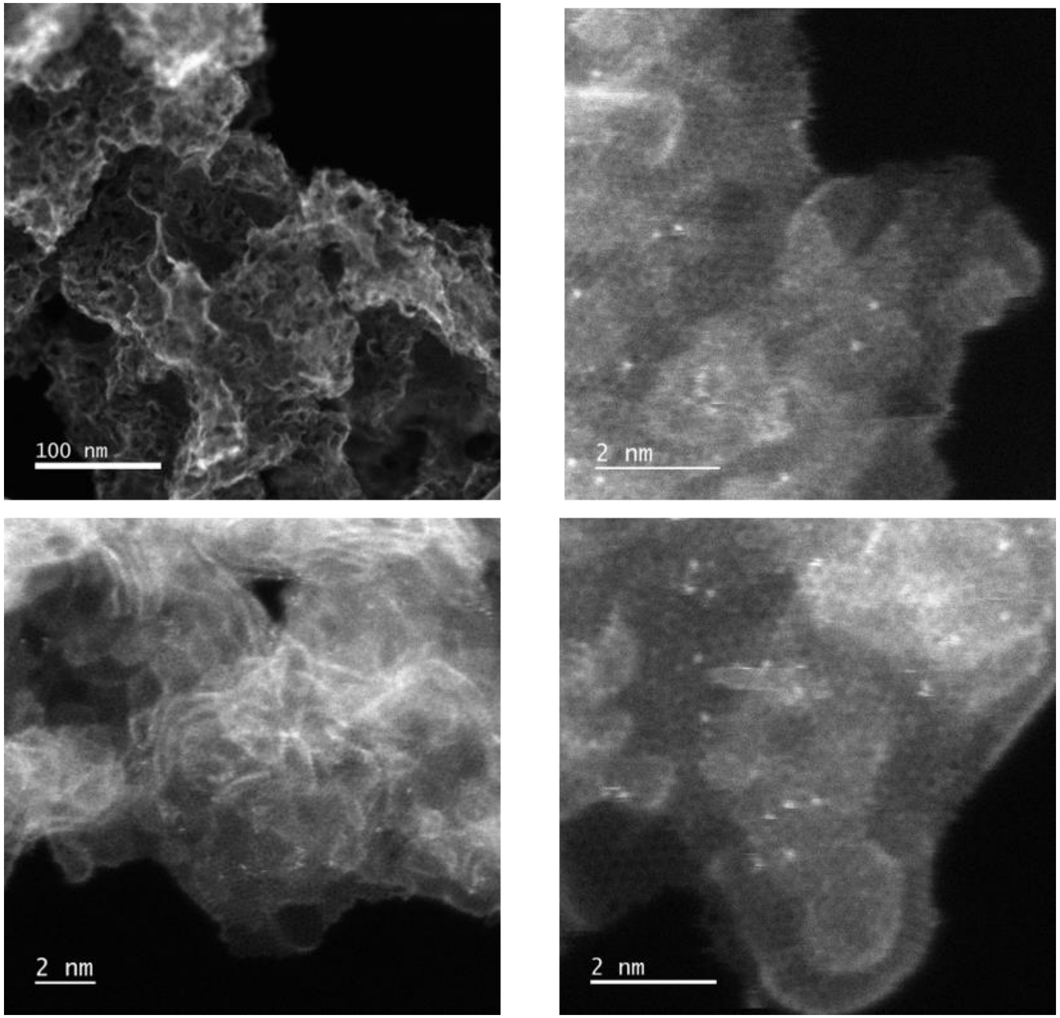
Fuel Cell Performance of Fe-N-C Gen-3 Catalysts





Gen-3 catalyst shows much higher performance at both 0.9V and 0.2V (data non-iR$_{corrected}$)

Accomplishments and Progress



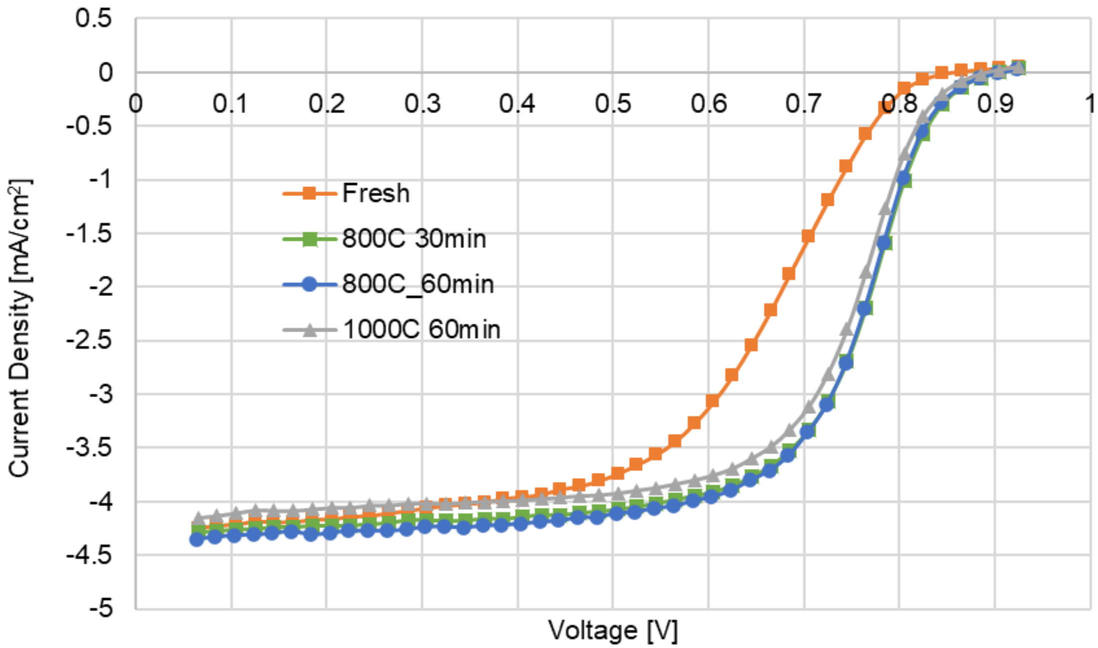
High throughput optimization of NH_3 treatment was done at ANL on 50g single batch Fe-N-C provided by PP. More than 30 samples were prepared and evaluated.

Microscopy by Dr. David Cullen (ORNL)

High throughput ammonia treatment by Dr. Magali Ferrandon and Dr. Debbie Myers (ANL)

Accomplishments and Progress

RDE Performance of Fe-N-C Gen-3.X Catalysts (ANL)



Ink recipe:
- ✓ 0.6 mg/cm^2
- ✓ Catalyst: 5mg, IPA: 0.5ml, D520 Nafion: 10µl

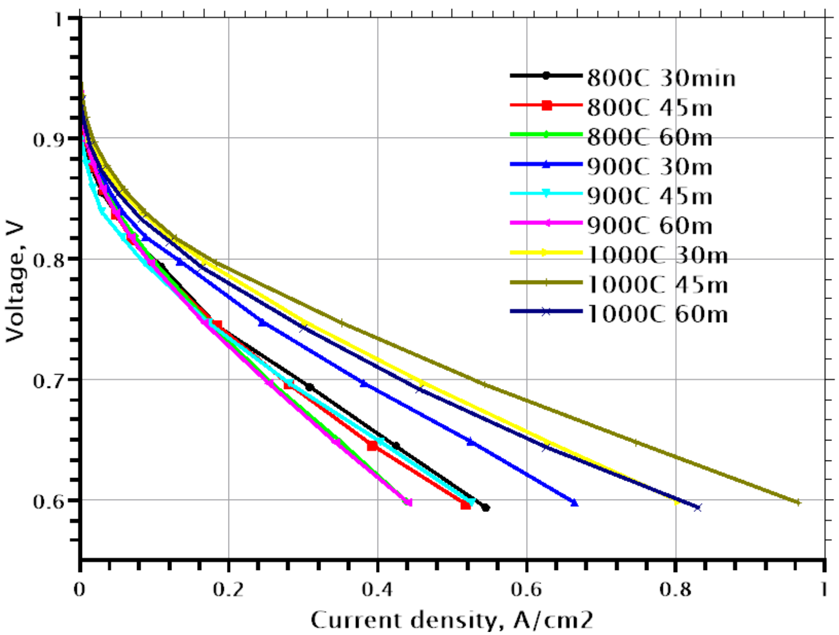
RRDE measurement protocol:
- ✓ 900 RPM
- ✓ O_2 saturated H_2SO_4
- ✓ Ag/AgCl reference electrode calibrated vs RHE
- ✓ Graphite rod as a counter electrode
- ✓ Voltage Stair-Step: 0.95V→0.05V→0.95V, 20mV step, 10s hold

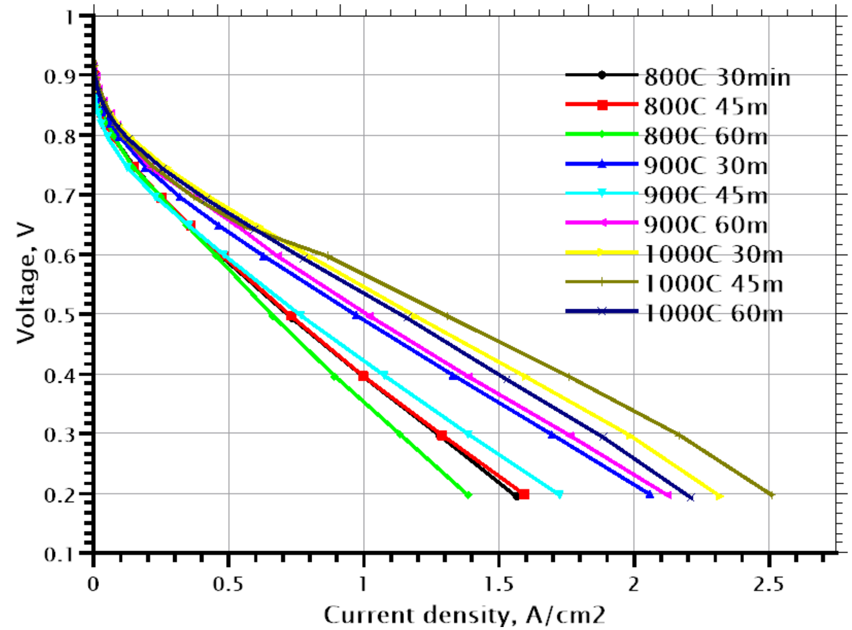
“Fresh” (after 2 synthetic steps of 5) has intrinsically low activity. Substantial increase in activity after NH_3 treatment

High throughput ammonia treatment, RRDE by Dr. Debbie Myers and Dr. Magali Ferrandon (ANL)

Accomplishments and Progress

Fuel Cell Performance of Fe-N-C Gen-3.X Catalysts (ANL)





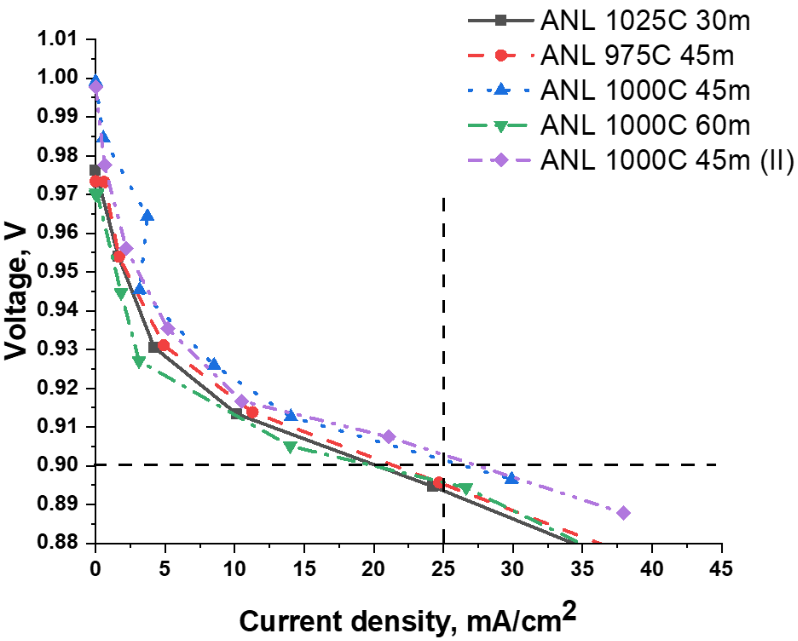
Conditions: A/C H_2/O_2 500/500 ml cm^{-2}, 100% RH, $150kPa_{backpressure}$, T_{cell}=80C.

Gen 3.A catalyst reached ~1 A/cm² at 0.6V and 2.5 A/cm² at 0.2V

High throughput ammonia treatment, data analysis by Dr. Debbie Myers and Dr. Magali Ferrandon (ANL)

Accomplishments and Progress

Fuel Cell Performance and Progress Towards 1st Go-no-Go Decision



Catalyst	Varied synthetic parameters	Current density at 0.9V (mA/cm^2)
Gen-1	Pipemedic acid as N-C precursor	2
Gen-2	Nicarbazin as N-C precursor	9
Gen-3.A	Nicarbazin as N-C precursor with ammonia treatment	20-27
Gen-3.B	Using ZIF-8 as a particle/pore forming	25

Conditions: A/C H_2/O_2 500/500 ml cm^{-2}, 100% RH, $150kPa_{backpressure}$, T_{cell}=80C.

Team successfully met 1st Go-no-Go design point:
25 mA/cm^2 at 0.9V (ElectroCat conditions)

High throughput ammonia treatment, data analysis by Dr. Debbie Myers and Dr. Magali Ferrandon (ANL)

Reviewers Comments

Comment: *More planned interactions with ElectroCat could be beneficial.*

Answer: Team actively collaborates with ElectroCat as well as planning to continue this collaboration (see Collaboration and Future Plans).

Comment: *The approach does not include a significant effort to develop a new catalyst.*

Answer: In the 1st year Pajarito developed ~25 new catalysts among 3 generations using proposed approach. The variables were: organic precursors, types of pore formers, heat treatment and post treatment parameters.

Comment: *The team should include specific stability and durability targets in addition to the performance milestones.*

Answer: Team actively participates in ElectroCat workshops and online meetings and will adopt new targets for the stability and durability.

Collaborations

- Established materials exchanged with US manufacturers of ionomers and membranes (Chemours, 3M and Tetramer).
- Team collaborates internationally with EU funded projects PEGASUS and CRESCENDO as a provider of commercial Fe-N-C catalysts and member of their Scientific Advisory Boards.
- Close collaboration with Dr. Andrei Kulikovsky on modeling of EIS and FC data.
- Team actively collaborated with ElectroCat consortium: ANL (high throughput synthesis of ammonia treated Fe-N-C catalysts; characterization, Machine Learning), ORNL (microscopic study of different generations of catalysts), LANL (evaluation of number of active sites and TOF by probing experiments), NREL (electrode and catalyst layer design).

Remaining Challenges and Barriers

- Increasing the number of active sites through creation of highly defective Fe-N-C structure.
- Decreasing the particle size of primary Fe-N-C catalyst (~600nm now). Target <300nm.
- Increasing catalyst stability and MEA durability for both as prepared Fe-N-C and ammonia treated Fe-N-C catalysts.
- Increasing proton conductivity in the thick catalyst layer through the uniform three-phase interface creation.
- Compile all produced data into the database for the usage in Machine Learning applications.

Proposed Future Work

- PP: a) optimization of zinc and b) ZIF-8 synthetic parameters (using Nicarbazin instead of phenanthroline). **Initiated**
- IRD: a) manufacture Gen-3.X MEAs for screening and b) optimize ionomer/membrane for best performer of Gen-3. **Done 50%**
- HNEI: a) screen activity Gen-3, b) EIS study on best performer and c) initiate a probing experiments with NO. **Done 40%**
- Based on the results obtained from IRD and HNEI re-formulate catalysts morphology and surface chemistry at PP
- Team: continue collaboration with ElectroCat consortium (ANL, ORNL, LANL and NREL)
- Apply high throughput synthesis and Machine Learning for enhanced rational design of Fe-N-C catalysts

Any proposed future work is subject to change based on funding levels

Technology Transfer Activities

- New generations of Fe-N-C catalysts will be commercially available after internal QC/QA.
- Pajarito jointly with General Graphene, Corp (TN, USA) applying for alternative funding in order to use Fe-N-C materials in DMFC application.
- Pajarito and IRD Fuel Cells, LLC looking for enhancing joint provisional application with novel electrode structure (pending).
- Pajarito exploring possibilities for alternative commercial application of Fe-N-C catalysts (2 US and 2 EU companies are approached).

Any proposed future work is subject to change based on funding levels

Summary

- 25 different catalysts were synthesized on batch level of 35-50g.
- More than 275 industrial quality MEAs were manufactured by IRD on $25 cm^2$ form-factor.
- HNEI and PP established activation protocol with minimal initial performance degradation.
- HNEI initiated comprehensive electrochemical analysis of Gen-1, 2 and 3.X MEAs manufactured by IRD.
- ~20 Fe-Mn-N-C, Fe-Zn-N-C and Fe-N-C (Urea) catalysts were synthesized, integrated into CCMs and 40 MEAs delivered to Pajarito and HNEI (under) evaluation.
- Team achieved 22-27 mA/cm^2 at 0.9V (silica) and 25 mA/cm^2 at 0.9V (ZIF-8).
- **3 joint publications for 1st year**, 3 oral presentations, including one invited
    - **Team met all Milestones and 1st Go-no-Go design point**

Technical Back-up Slides

Technical Back-up

Publications and Presentations

Publications:

[1] T. Reshetenko, G. Randolf, M. Odgaard, B. Zulevi, **A. Serov***, A. Kulikovsky "The Effect of Proton Conductivity of Fe–N–C–Based Cathode on PEM Fuel cell Performance" Journal of The Electrochemical Society 167 (2020) 084501.

[2] C.L. Vecchio, **A. Serov***, H. Romero, A. Lubers, B. Zulevi, A.S. Aricò, V. Baglio "Commercial platinum group metal-free cathodic electrocatalysts for highly performed direct methanol fuel cell applications" J. of Power Sources 437 (2019) 226948.

[3] T. Reshetenko, **A. Serov**, A. Kulikovsky, P. Atanassov "Impedance Spectroscopy Characterization of PEM Fuel Cells with Fe-NC-Based Cathodes" J. of The Electrochemical Society 166 (2019) F653-F660.

Presentations:

[1] A. Serov*, G. McCool, H. Romero, S. McKinney, A. Lubers, M. Odgaard, T. V. Reshetenko, B. Zulevi "*PGM-Free Oxygen Reduction Reaction Electrocatalyst: From the Design to Manufacturing*", ECS Meeting 235, Dallas, TX (2019).

[2] A. Serov*, G. McCool, H. Romero, S. McKinney, A. Lubers, M. Odgaard, T. V. Reshetenko, B. Zulevi "*Are PGM-free Fuel Cell Catalysts Ready for Prime-Time?*", EFCD2019, La Grand Motte, France (2019). **Invited.**

[3] A. Serov*, G. McCool, H. Romero, S. McKinney, A. Lubers, M. Odgaard, T. V. Reshetenko, B. Zulevi "VariPore™: A Powerful Manufacturing Platform for Fuel Cell and Electrolyzer Applications", ECS Meeting 236, Atlanta, GA (2019).

[4] T. Reshetenko, **A. Serov**, A. Kulikovsky, P. Atanassov, "*Comprehensive characterization of PGM-free PEM fuel cells using AC and DC methods*", ECS Meeting 236, Atlanta, GA (2019).

Progress: MEA Preparation

Hot pressing conditions were harmonized around 3 groups (Pajarito, IRD Fuel Cells and HNEI):

- Press temperature of 140^{o}C
- Press time of 4 minutes
- Press at ~2400lbs
- Cathode gasket thickness is 10mil. Anode gasket thickness is 6mil. Compression ratio was in the range of 15-20%.
  - Gaskets are supposedly rigid and non-compressible
  - No variations in gasket thickness
  - GDL used is Freudenberg H23C8 (220-230um thick)

Progress: Activation Protocol

PAJARITO POWDER
FUEL CELL CATALYSTS

Activation Protocol was harmonized at 2 groups (Pajarito and HNEI), while IRD Fuel Cells makes additional optimization:

- MEA placed in the hardware (Fuel Cell Technology) either 25cm^2 (CCMs made by IRD) or in 5cm^2 (CCSs made by Pajarito)
- Cell's temperature increased to 80ºC with no gases flowing
- When temperature stabilizes, fully humidified gases supplied to the anode (H_2 500ml cm^{-2}) and cathode (O_2 500ml cm^{-2})
- Backpressure adjusted to 150kPa
- After 10 minutes polarization curves recorded from OCV to 0.6V (5 scans)
- Full polarization curves recorded from OCV to 0.2V (2 curves)

HiSERF

HAWAII SUSTAINABLE ENERGY RESEARCH FACILITY
A University of Hawaii – Hawaiian Electric Company Partnership
Sponsored by
Office of Naval Research and U.S. Department of Energy

IRD